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NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Fibres, Foils and Coatings

5 We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, of Leverkusen-Bayerwerk, Germany, a body corporate, organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a method for making highly elastic shaped elements and more particularly to a method of making polyurethane fibres, foils and coatings.

15 It has heretofore been known to react an isocyanate - modified polyhydroxy compound with a glycol, a diamine or water in the presence of a solvent and to shape the resulting solution into a foil or fibre. The reaction with diamines results in articles having good elastic properties but it is extremely difficult to carry out this reaction on a commercial scale because of the extremely high reaction velocity between isocyanates and amines which frequently leads to premature gel formation of the solution.

25 It has also been known to react a dicarboxylic acid dihydrazide or a carbodihydrazide with a diisocyanate. The polycondensate thus obtained do not possess the highly elastic properties of known polyurethanes or polyureas. Further, the thermal instability of these polycondensates makes it necessary to carry out the reaction in a solvent. When an attempt is made to carry out this reaction on a commercial scale, the low solubility of the resulting polycondensates presents great difficulties and the solutions are unstable.

40 It has also been known to prepare casting compositions by reacting at high temperatures isocyanate modified polyesters with compounds such as dihydrazides, substituted-bis-semi-carbazides and dioximes to obtain elastomeric shaped elements after a relatively long final heating at about 100° C. This process

does not lend itself to the production of filaments or foils for the reason that the long heating time necessary to cure the castings cannot be applied to the preparation of filaments or foils on a commercial scale. Moreover, these casting compositions are made with an excess of polyisocyanate. Even if the reaction is performed in two steps the sum of isocyanate groups altogether is an excess over the hydrazide groups. The resulting cross-linked plastic is no longer soluble. The final chemical reaction is done after the film or foil has been formed, that is after or at least during the elimination of the solvent in the case where the casting is made in solution.

It is therefore an object of this invention to provide an improved method of making polyurethane fibres, foils and coatings. It is another object of this invention to produce polyurethane fibres, foils and coatings having excellent elastic properties. It is still another object of this invention to provide a method of making polyurethane fibres, foils and coatings from readily defoamable stable solutions. It is a further object of this invention to provide a method of making highly elastic filaments having very high tensile strength, high elongation, low permanent elongation and a high modulus. It is a still further object of this invention to provide a method of making a clear, highly elastic polyurethane foil having high tensile and tearing strength. It is still another object of this invention to provide a method of making polyurethane coatings having good bonding power; high elasticity to abrasion and good light fastness. It is still another object to provide a storage stable composition for the preparation of polyurethane fibres, foils and coatings, which composition is not subject to premature gel formation. It is still another object of this invention to provide for a chemical reaction in solution in which the product is held after the reaction has been finished and from which the final

shape may be given to the product without further chemical reaction.

- 5 The foregoing objects are accomplished by providing a method for making highly elastic fibres, foils and coatings by the polyisocyanate polyaddition process wherein a substantially linear isocyanate - modified organic compound containing terminal NCO groups (which has been prepared by reacting an excess of an organic diisocyanate with an organic compound containing active hydrogen atoms which are reactive with —NCO groups and having a molecular weight of from 700 to 5,000) is reacted in an inert solvent with a solution of a dihydrazide having the general formula



- 20 wherein A is a CO, CS or SO₂ group; R and R¹ each represent a hydrogen atom, an alkyl radical or an aryl radical, with the proviso that at least twice in the molecule R and R¹ represent a hydrogen atom; Z is an alkylene radical, the chain of which may be interrupted by one or more hetero atoms such as oxygen or sulphur, an arylene radical, an aralkylene radical, an NH—, NH—NH, O—Y—O or NH—Y—NH group, wherein Y in the last two formulae is a divalent organic radical, and n is 0 or 1, the dihydrazide being employed in a quantity of from 100 mol per cent to 110 mol per cent of that required to react with the —NCO groups present and thereafter removing the solvent from the solution while effecting shaping into the desired final object.
- 35 This procedure produces in a short time solutions having a concentration permitting deformation into shaped articles such as filaments and foils which exhibit excellent elastic properties.

- 40 Any suitable organic compound containing active hydrogen atoms which are reactive with —NCO groups and which are determined by the Zerewitinoff test may be reacted with an organic polyisocyanate to produce an isocyanate - modified compound for use in the process of this invention such as, for example, hydroxyl polyesters, polyester amides, polyhydric polyalkylene ethers, polyhydric polythioethers, polycarbonates, and polyacetals.
- 50 These compounds, having terminal hydroxyl groups and substantially linear structure, should have a molecular weight of from 700 to 5,000 and a melting point preferably lower than 60° C. and even more preferably lower than 45° C. for the reason that the elastic properties, especially at low temperatures, decrease because of hardening.

- 60 Any suitable hydroxyl polyester may be used for the preparation of the isocyanate modified active hydrogen compound, such as, those prepared from dihydric alcohols and dicarboxylic acids. Any suitable dicarboxylic acid may be used such as adipic acid, glutaric acid, azelaic acid, sebacic acid, nonanedicarboxylic acid, thiodipropionic acid, pimelic acid, ricinoleic acid, suberic acid, fumaric acid, maleic acid, phthalic acid and the like. Any suitable dihydric alcohol may be used such as, for example, ethylene glycol, 1,3 - propylenediol, dimethyl propane - 1,3 - diol, 1,4 - butanediol, 1,6 - hexanediol, 2,5 - hexanediol, 1,10 - decanediol, thiodiglycol, diethylene glycol, triethylene glycol, 4,4' - dihydroxy dicyclohexyl dimethyl methane, N - methyl diethanolamine, and the like. Further suitable polyesters can be obtained from caprolactones and glycols such as 1,4-butane diol.

Owing to the greatly improved resistance to hydrolysis, the polyesters prepared from glycols having at least 5 carbon atoms and which are transformed with less than equivalent quantities of diisocyanates into polyester urethanes are preferred. A typical example of such a composition is a polyester of hexanediol and adipic acid having a molecular weight of 1,000 which is transformed with 1/2 mol of toluylene diisocyanate into a polyester urethane having a molecular weight of about 2,200. Of course, mixtures of the aforementioned polyester starting materials may be employed.

Any suitable polyester amide may be used such as those prepared by the incorporation of amino alcohols, amino carboxylic acids and polyamines into the formulations for hydroxyl polyesters set forth above. Any suitable amino alcohols such as, for example, ethanol amine, propanol amine and the like may be used.

Any suitable polyamine, such as, for example, toluylene diamine, hexanediamine, piperazine, and the like may be used. Any suitable amino carboxylic acid such as, for example, ω-amino caproic acid and ω - amino undecanoic acid and the like may be used.

Any suitable polyalkylene ether may be used in the preparation of isocyanate modified active hydrogen containing compounds in accordance with this invention such as the reaction product of any of the above-mentioned polyhydric alcohols with alkylene oxides such as, for example, ethylene oxide, propylene oxide, butylene oxide, amylene oxide, and the like. Of course, the polyhydric polyalkylene ethers can be prepared from other starting materials such as, for example, tetrahydrofuran, epibromohydrins such as, for example, epichlorohydrin and the like as well as aralkylene oxides such as, for example, styrene oxide and the like. The polyhydric polyalkylene ethers may have either primary or secondary hydroxyl groups and preferably are polyhydric polyalkylene ethers prepared from alkylene oxides having from two to five carbon atoms such as, for example, polyethylene ether glycols, polypropylene ether glycols, polybutylene ether glycols, and the like. The polyhydric polyalkylene ethers may be prepared by any known process such as, for example, the process disclosed by Wurtz in 1859 and in *En-*

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wherein A is a CO, CS or SO₂ group; R and R¹ each represent a hydrogen atom, an alkyl radical or an aryl radical, with the proviso that at least twice in the molecule R and R¹ represent a hydrogen atom; Z is an alkylene radical, the chain of which may be interrupted by one or more hetero atoms such as oxygen or sulphur, an arylene radical, an aralkylene radical, an NH—, NH—NH, O—Y—O or NH—Y—NH group, wherein Y in the last two formulae is a divalent organic radical, and n is 0 or 1, the dihydrazide being employed in a quantity of from 100 mol per cent to 110 mol per cent of that required to react with the —NCO groups present and thereafter removing the solvent from the solution while effecting shaping into the desired final object. This procedure produces in a short time solutions having a concentration permitting deformation into shaped articles such as filaments and foils which exhibit excellent elastic properties.

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cyclopedia of Chemical Technology, Vol. 7, pp. 257—262, published by Interscience Publishers, Inc. (1951) or in United States Patent Specification No. 1,922,459.

5 Any suitable polyhydric polythioether may be used such as, for example, the condensation product of a thiodiglycol or the reaction product of a polyhydric alcohol such as is disclosed above for the preparation of the hydroxyl polyesters with any other suitable thioether glycol. Other suitable polyhydric polythioethers are disclosed in United Kingdom Patent Specification No. 819,384 and in United States Patent Specification No. 2,900,368.

15 Any suitable polyacetal may be used such as, for example, the reaction product prepared by reacting an aldehyde with a polyhydric alcohol. Any of the polyhydric alcohols mentioned above may be used. Any suitable aldehyde may be used such as, for example, formaldehyde, polymers of formaldehyde, acetaldehyde, butyraldehyde and the like. The polyacetals described in United Kingdom Patent Specifications Nos. 798,209 and 840,097 are suitable for use in the preparation of the isocyanate modified polyhydroxy compound in accordance with this invention. Any of these compounds containing active hydrogen containing groups when reacted with an excess of an organic polyisocyanate are suitable in the practice of this invention to prepare isocyanate modified polyhydroxy compounds.

30 Any suitable hydroxyl-terminated polycarbonate such as, for example, those set forth in United Kingdom Patent Specifications Nos. 772,627 and 808,488 and in Canadian Patent Specification No. 594,805 may be used. Further, the polycarbonates obtained from cyclic carbonates and glycols and those hydrocarbon polymers which contain small quantities of hydroxyl groups can likewise be used as starting materials.

35 The polyhydroxy compounds can be used singly or mixtures thereof can be reacted with diisocyanates, it being preferred to use 1.75—4 mols and preferably about 2 mols of diisocyanate per mol of polyhydroxy compound. In this case, with a molar ratio of polyhydroxy compound to diisocyanate of 1:2, compounds are formed with which there is still a certain linking of the individual molecules of the polyhydroxy compound, but free —NCO groups occur at the ends.

45 With a molar ratio of exactly 1:2, merely the ends of the chains of the polyhydroxy compounds are provided by way of urethane groups with free —NCO groups, whereas with molar ratios greater than 1:2, free diisocyanate is present in addition to those compounds of high molecular weight which carry isocyanate groups. This reaction can be effected in known manner by dehydrating the polyhydroxy compound by heating it for approximately one hour *in vacuo* at 130° C. and reacting the dehydrated polyhydroxy compound

with the diisocyanate at an elevated temperature of, for example, from 80° C. to 130° C. Alternatively, a solution of the diisocyanate in an inert solvent such as methylene chloride, acetone or benzene may be added to the polyhydroxy compound. The temperature of the mixture is slowly raised while distilling off the solvent and the reaction is allowed to proceed for a sufficient time (about 1—2 hours) at an elevated temperature (preferably 90° C. to 110° C.).

70 The reaction may also be effected in the presence of a small quantity of a trifunctional alcohol (less than 5% of the OH number of the polyhydroxy compound), such as trimethylol ethane or trimethylol propane or trifunctional isocyanates, in which case the reaction should lead only to such weakly branched products that a gel formation does not occur.

80 Any suitable organic diisocyanate may be used in the process of this invention to produce isocyanate-modified polyhydroxyl compounds such as, for example, 1,4-phenylene diisocyanate, 4,4'-diphenyl diisocyanate, 4,4'-diphenyl methane diisocyanate, 4,4'-diphenyl-dimethyl methane diisocyanate, dibenzyl diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate and mixtures of 2,4- and 2,6-tolylene diisocyanate, 1,4-cyclohexane diisocyanate, hexamethylene diisocyanate, 4,4'-hexahydrodiphenyl methane diisocyanate, naphthalene-1,5-diisocyanate, furfurylidene diisocyanate, 1,5-"Tetralin" (registered Trade Mark) diisocyanate, di-(3-isocyanato-4-methyl phenyl)-urea, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 3,3'-dimethoxy- or 3,3'-dichloro-4,4'-diphenylmethane diisocyanate, 2,2'-diethyl-4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-diphenyl diisocyanate, 1-methyl-3,5-diethyl-2,4-phenyl diisocyanate, diphenylether-4,4'-diisocyanate, stilbene diisocyanate, 4,4'-diphenylsulphide diisocyanate, xylene diisocyanate, dicyclohexylmethane diisocyanate and the like. The symmetrical diisocyanates are preferred. The products prepared from 4,4'-diphenyl dimethylmethane diisocyanate and hexamethylene diisocyanate have excellent stability to light.

100 The substantially linear, isocyanate-modified polyhydroxy compounds are preferably transformed into approximately 50% solutions by the addition of solvents which also dissolve polyacrylonitrile and which are neutral with respect to —NCO groups. The solvent is preferably added at room temperature or at slightly elevated temperature. The resulting solutions are reacted, if necessary after further dilution with a dilute substantially 1—10% solution of the compounds having the aforementioned general formula.

105 The suitable solvents being known to dissolve polyacrylonitrile are strongly polar

liquids and usually contain amido or sulphoxide groups. They exhibit a strong tendency to form hydrogen bonds. They include dimethyl formamide, dimethyl acetamide, dimethyl propionamide, tetramethylene sulphone, N-methyl pyrrolidone, dimethyl sulphoxide, hexamethyl phosphorous amide and the like. These solvents may be blended with other solvents such as dioxane, tetrahydrofuran, glycol methylether acetate, ethyl acetate, acetone, chlorobenzene, cyclohexanone, methylene chloride and chloroform, which under the reaction conditions have to be inert to —NCO groups.

Any suitable compound complying with the general formula set forth above such as, for example, carbodihydrazide, N,N'-dimethyl carbodihydrazide, 1,5-diphenylcarbodi-hydrazide, thiocarbodihydrazide, sulphodi-hydrazide, dicarboxylic acid dihydrazides (e.g. the dihydrazides of oxalic acid, adipic acid, sebacic acid, thiodipropionic acid, disulphonic acid, such as 1,3- or 1,4-phenylene disulphonic acid hydrazides), cyclobutane-1,2-dicarboxylic acid dihydrazide, cyclohexane-1,3- and cyclohexane-1,4-dicarboxylic acid dihydrazide, ethylene-bis-semi-carbazide, tetramethylene-bis-semicarbazide, 1,4-phenylene-bis-semicarbazide, piperazine dicarboxylic acid dihydrazide, di-semi-carbazides and dithiodisemicarbazides (e.g. 1,6-hexamethylene bis-semicarbazide), bis-hydrazine carboxylic acid esters of glycols

such as 1,4-butanediol, 1,6-hexanediol or 1,4-phenylene bis-hydroxyethyl ether and N,N'-diaminobisurea and hydrazodicarboxylic acid dihydrazide. Mixtures of dihydrazide compounds can also be used.

In order to regulate the molecular weight of the products obtained by the process according to the present invention, the dihydrazide compounds of the aforementioned general formula may be reacted together with a small quantity, preferably 0.1-4% of a monofunctional acid hydrazide. The use of the dihydrazide compound in a slight excess with respect to the quantity corresponding to the —NCO content results in a product of lower molecular weight. If the dihydrazide compound is employed in a smaller quantity than the equivalent of the —NCO content, products of higher molecular weight are obtained with initiation of cross-linking. An initiation of cross-linking is, however, permissible only to such a degree that the product remains dissolved.

In order to carry out the reaction, a solution of the dihydrazide compound, which may be heated if necessary, is quickly stirred into a thinly liquid solution of the isocyanate-modified polyhydroxy compound which is stirred at high speed. After a short time there is an increase in viscosity with formation of the final product which is of high molecular weight and which contains atom groupings of the following type:



where R, R', A and Z have the meaning set forth above.

A solution of the dihydrazide compound can also be added dropwise to a solution of the isocyanate-modified polyhydroxy compound. Alternatively a solution of the two components may be combined continuously or intermittently in a suitable mixing apparatus. It is also possible to introduce the solution of an isocyanate-modified polyhydroxy compound into a solution of the dihydrazide compound. The solutions which are obtained are clear, colourless, or practically colourless solutions having a viscosity of about 1-800 poises/20° C., a solid content of about 10-40% and are completely stable. In order to obtain products from low viscosity to relatively high viscosity, the solutions can also be concentrated by evaporation, for example at 60-80° C. *in vacuo*. Pigments and fillers, for example, titanium dioxide, and also light and oxidation stabilisers and heavy metal complex formers can also be introduced into the solutions.

The shaping from the solution can for example be effected by means of nozzles or spinnerets. The solution, for example a dimethyl formamide solution having a viscosity of about 1-800 poises/20° C. is spun into

hot water or aqueous solvent mixtures and the filament is allowed to coagulate to its maximum strength, if necessary, by standing in hot water. Alternatively, solutions having a viscosity of 50-800 poises/20° C. are spun through a tunnel having a length of several meters and which is heated to about 150-250° C. The filaments which are formed with evaporation of the solvent are wound, if necessary after injecting talcum into the tunnel and/or after applying talcum. In certain circumstances, the elastomeric filaments can be further stretched to about 1.1-3 times their length over a short heating zone at about 130-200° C., the modulus of the filaments generally rising with decreasing total elongation. By heating to temperatures of about 100-170° C., this stretching or elongation can if necessary be fixed. Generally speaking, however, such an after-treatment can be dispensed with since the products obtained by the present process already have high moduli. The filaments are stable, colourless and, if the starting materials are suitably chosen, they are products which are very resistant to hydrolysis, have an elastic elongation of 400-900%, a relatively high modulus and excellent tensile strength. They are suitable as textile materials since they are resistant to abrasion

and are stable with respect to solvents which are used for cleaning fabrics. Furthermore, the combined elastic and mechanical properties of the products are outstanding. For example, they show only a small permanent elongation, only a very small decrease in tension under load, very little "stretch" under a suspended load and a good stress-strain behaviour. Since they can be spun in monofilar or multifilar form with high small filament thicknesses from about 4 den. up to filaments of about 500 den., they are very suitable for the manufacture of elastomeric fabrics of low weight and high restoring power, such as are particularly required in the corsetry industry, for the manufacture of medical articles and for many elastic everyday articles such as bathing costumes and sports clothing.

Highly elastic foils can be obtained from the solutions by means of suitable casting devices with evaporation of the solvent. They are clear, light in colour, highly elastic with a high modulus, have high tensile and tearing strength and possess a good non-tacky surface. Shaped elements can also be produced by dipping processes. By application of the solutions to textile supports and evaporating the solvent, excellent coatings are obtained which are non-tacky on the surface, can be deformed with high elasticity and have good resistance to hydrolysis and very good resistance to light. This invention constitutes a very important technical advance over known coatings of polyisocyanates and polyhydroxy compounds from two component systems since coatings are obtained from a stable prepared solution merely by removing the solvent and the problem of the so-called "pot" time is overcome.

The invention is further illustrated by the following Examples in which the parts are by weight unless otherwise specified.

EXAMPLE 1

A solution of about 59 parts of 4,4'-diphenyl methane diisocyanate in 250 ml. of anhydrous benzene is added to 300 parts of a polytetramethylene glycol ether having a molecular weight of about 2540 and an hydroxyl number of 44, the molar ratio being about 1:2. The resulting mixture is stirred on a boiling water bath while passing over nitrogen for about 1 hour with the solvent being distilled off. The mixture is then heated for about 2 hours at about 100° C. The addition product, after cooling to about 40° C. is stirred with about 360 parts of pure dimethyl formamide. The isocyanate content of the solution is about 1.37% —NCO.

About 150 parts of the 50% solution of the polyether isocyanate are diluted with about 200 parts of dimethyl formamide. A solution of about 2.20 parts of carbodihydrazide, which is about an equimolar quantity to the isocyanate compound, in about 110 parts of dimethyl formamide is added at a temperature of approximately about 70° C. while stirring vigorously. The addition is effected within 10 seconds. A short time afterwards, the viscosity of the solution increases and a practically colourless, smoothly discharging, substantially 17% solids, stable solution having a viscosity of 70 poises/20° C. is obtained. This solution can be drawn into filaments.

The solution thus obtained is spun with a delivery quantity of 1.2 ml./min. through a 12-aperture spinneret provided with holes having a diameter of 0.15 mm. into a water bath at a temperature of about 90° C. and having a length of about 2 meters. The highly elastic filament thereby easily obtained is wound onto a spool at a speed of about 10 m/min. After standing in hot water at a temperature of 50—70° C. the filament is dried and shows the following properties:

Count: 98 den.

Tensile strength: 0.80 g./den. related to original count
8.35 g./den. related to count on breaking

Elongation: 750%

Permanent elongation: 2.2% measured after elongation by
100% with an elongation speed of
100% min., loading for two minutes
and relaxation for 30 seconds

Modulus (100%): 0.060 g./den.

Decrease in tension: 8.3% after stretching the filament
to 100% with a speed of 100%/min.
and a stationary period of 2 minutes

Even after treatment for 14 hours with boiling, 5% soda solution,
the following values are still obtained:

Count: 84 den.

Tensile strength: 0.69 g./den. related to original count

Elongation: 840%

Permanent elongation: 3.0%

Decrease in tension: 5.0%

5 If the solution is poured onto a sheet of glass, clear colourless films are obtained after drying at about 100° C., these films being of high elasticity, pliability and having non-tacky surface properties, and also having very high tensile strength and tearing strength values.

EXAMPLE 2

10 About 400 parts of the reaction product of 1 mol of a polyester of butane - 1,4 - diol, hexane - 1,6 - diol and adipic acid and 1/2 mol toluylene diisocyanate and having a molecular weight of 2,160 are reacted with about
15 103 parts of 4,4'-diphenyl dimethyl methane diisocyanate in about 300 ml. of benzene. After distilling off the solvent and thereafter heating for about 2 hours at about 100° C., a polyester isocyanate containing about 2.79%
20 of free isocyanate groups is obtained. After incorporating about 500 g. of dimethyl formamide while stirring, a 50% solution is obtained which contains about 1.36% of —NCO.

25 To about 150 parts of this solution, after being diluted with about 200 parts of dimethyl formamide, are added all at once and while stirring well, 2.18 parts, the equivalent quantity, of carbodihydrazide dissolved hot in 175 parts of dimethyl formamide. A smoothly
30 running solution which can be satisfactorily stirred is thereby obtained after a short time with an increase in viscosity. The resulting solution has a viscosity of about 115 poises/

20° C. and a solid content of about 14.7%.

Spinning is carried out as described in Example 1. Highly elastic 100 den. filaments
35 having a tensile strength of 0.83 g./den., original count, an elongation of 570%, a permanent elongation of 4.9% and a modulus (100%) of 0.062 g./den. are obtained with
40 high spinning certainty.

Foils which are obtained by pouring these materials onto sheets of glass and evaporating off the solvent show an excellent resistance to light and hydrolysis and at the same time have
45 very good elastic properties. Thus, a foil without any additions does not show any discoloration and has an unchanged non-tacky surface after being kept for about 110 hours in a
50 "Weatherometer" with simultaneous irradiation with ultra-violet light.

EXAMPLE 3

About 150 parts of the polyester isocyanate solution prepared as described in Example 2 and the —NCO content of which has fallen
55 to 1.18% after standing for 24 hours, are diluted with about 150 parts of dimethyl formamide. About 3.43 parts of adipic acid dihydrazide, a quantity equivalent to the —NCO content, in about 140 parts of dimethyl formamide is added in the form of a practically
60 boiling solution while stirring vigorously and after the first-mentioned solution has been cooled to about +3° C. A completely colourless, approximately 19% solids solution is
65

formed which has a viscosity of 70 poises/20° C. The solution remains colourless and unchanged as regards viscosity after being kept for several months.

The solution is spun into hot water under the conditions described in Example 1, whereby elastic filaments having the following properties were obtained:

5

Count: 119 den.

Tensile strength: 0.69 g/den.

Elongation: 540%

Permanent elongation: 6%

Modulus (100%): 0.053 g./den.

- 10 Clear foils having good properties can also be obtained from this solution.

EXAMPLE 4

- 15 About 165 parts of an ethylene glycol-adipic acid polyester having an hydroxyl number of 53.5 are dehydrated for about 1 hour *in vacuo* at about 130° C. and then a solution of about 46.8 parts of 4,4'-diphenyl methane diisocyanate, in a molar ratio 1:2.36 in 250 parts of methylene chloride is added, the solvent is 20 distilled off and thereafter the polyester is heated for about 2 hours at about 100° C. After adding about 635 parts of dimethyl formamide, the —NCO content of the solu-

tion is established as being 0.661% —NCO.

About 413 parts of the polyester isocyanate 25 solution are cooled to about +10° C. and a solution of about 3.1 parts of carbodihydrazide and about 0.89 parts of hexamethylene - bis-semi - carbazide 90% and 10%, respectively, of the quantity calculated on the —NCO 30 equivalence, in about 80 parts of dimethyl formamide is added, the latter solution being at a temperature of about 65° C. The viscosity increases in a short time with a rise in temperature to about 31° C. The substantially 35 20.6% solids solution thus obtained was spun to give colourless highly elastic filaments having the following properties:

Count: 182 den.

Tensile strength: 0.52 g./den.

Elongation: 682%

Permanent elongation: 4%

Modulus (100%): 0.049 g./den.

- 40 A foil obtained by casting the solution in a layer with a thickness of 1 mm. and evaporating the solvent shows the following properties,

among which the strength value, the modulus and the resistance to further tearing are particularly outstanding: 45

Thickness: 0.18 mm.

Tensile strength test (5.2 cm. rod test): 490—630 kg./cm²

Elongation: 710%

Tension value at 20% elongation: 10 kg./cm.

Tension value at 300% elongation: 150 kg/cm

Resistance to further tearing according to Graves: 50—88 kg/cm

Resistance to tearing by needle test: 63—69 kg/cm

Shore hardness: 62.7°

- 50 After pouring a sample of the solution into water, washing and drying the precipitated polymer 10 parts of it are dissolved in dimethyl formamide within 30 minutes at 50°

C. The relative viscosity is 1.92/25° C.

The 1,6 - hexamethylene - bis - semicarbazide is obtained in form of needles by catalytic reduction of the carbobenzoxy compound

(m.p. 68—69° C.) prepared from carbobenz-oxyhydrazine and 1,6 - hexamethylene diisocyanate (m.p. 168—169° C.).

EXAMPLE 5

5 About 350 parts of an ethylene glycol/adipic acid polyester having a molecular weight about 2,100 are reacted with about 84 parts of 4,4' - diphenyl methane diisocyanate in about 200 ml. of benzene as described in
10 Example 1 and dissolved in about 434 parts of dimethyl formamide. The 50% solution which is obtained contains 1.41% of free isocyanate groups.

15 About 150 parts of this 50% polyester isocyanate solution are mixed with an equivalent quantity, about 2.26 parts of carbodihydrazide in about 125 parts of dimethyl formamide as a solution at a temperature of about 60° C. A substantially 20.5% solids solution having a
20 viscosity of about 100 cP/20° C. is obtained with a rise in viscosity. When this solution is spun into hot water as described in Example 1, highly elastic filaments are obtained having a denier of 143, a tensile strength of 0.55 g./den., an elongation of 750% and a permanent
25 elongation of 3.5%. The modulus (100%) is 0.032 g./den. and the tension drop (100%) is 8.1%.

EXAMPLE 6

30 2800 Parts of a polyester prepared from ethylene glycol and adipic acid and having an OH number of 55.6 and an acid number of 1.85 are dehydrated *in vacuo* at 130° C. for 1 hour and then a solution of 556 parts of 4,4'-diphenyl methanediisocyanate in 840 parts of chlorobenzene is added and the mixture heated to 95—100° C. for 2 hours. After cooling the
35 reaction mixture has a viscosity of 350 poises/20° C. and an NCO content of 1.615%. 308 Parts of a solution of 1.73 parts of carbodihydrazide in 12.27 parts of water and 294 parts of dimethyl formamide are continuously reacted at room temperature with 100 parts of the above solution. From a container being
40

under a pressure of 8 atm. 100 g. per minute 45 of the polyester - isocyanate - solution are introduced by a gear pump into a head of a double screw running with 150 rotations per minute. At the same time 308 g/minute of the carbodihydrazide solution are injected by
50 means of an injection nozzle with a pressure of 120 atm. Through a third inlet a 50% pigment paste is added by a gear pump at a rate of 8 g/minute at the end of the first third of the double screw. 55

The pigment paste is prepared from 2 parts of titanium dioxide, 1 part of dimethyl formamide and 1 part of the above elastomer solution by mixing the ingredients in a ball mill for several hours. The paste can also be made
60 on a roller. After a time of say of about 30 sec. a 20% solution of an elastomer containing about 5% (calculated on the solid content) of pigment is obtained at the outlet of the double screw. The solution has a viscosity of 65 135 poises/20°.

If instead of the equivalent amount of carbodihydrazide solution (308 parts) an excess is injected viscosity and molecular weight of the elastomer solution are decreased. If 315 g. of
70 carbodihydrazide solution are employed the elastomer solution shows a viscosity of only 24 poises/20°. After the removal of the solvent the elastomer itself shows a relative viscosity (10 g/l) dissolved in hexamethyl phosphorous
75 amide of 2.41 and 1.95 respectively.

The elastomer solutions can be concentrated if desired by means of a film evaporator. A solution with a viscosity of 400 poises/20° and with a solid content of 25.7% is spun at
80 a rate of 12.9 g/minute through a spinneret with 24 nozzles of a diameter of 0.15 mm. into a 5 m. tunnel heated to 220° C. Air of 240° is blown into the tunnel as a counter stream. The multifil is wound at a rate of 85 200 m/min. after talcum has been applied onto the filaments. After removing the talcum by 10 minutes washing with water at 35° C. the following properties are observed.

Count: 138 den.

Elongation: 680%

90 Permanent elongation after 300% expansion and 30 sec. of relaxation: 10%

Modulus 300%: 1.167 g/den.

Tensile strength: 0.60 g/den.

Highly elastic filaments are also obtained by spinning into hot water in accordance with Example 1. The properties are similar to the above properties.

95 The elastomer solution can also be applied to a fabric by means of a doctor. After drying

at 100° C. a coating is obtained with high elasticity and high resistance against rubbings.

The solution can be cast onto glass plates. After evaporation of the solvent at 70—100° 100 C. highly elastic foils are obtained which exhibit the following properties.

Thickness: 0.20 mm.

Tensile strength: 490 kg/cm²

Elongation: 775%

Modulus 20%: 7 kg/cm²

Modulus 300%: 88 kg/cm²

Shore hardness: 59

Resistance to further
tearing acc. to Graves: 81 kg/cm

EXAMPLE 7

5 About 300 parts of a polyester urethane having a molecular weight of 2,000 and prepared from 1 mol of hexanediol/adipic acid polyester having a molecular weight of 900 and 0.5 mol of toluylene diisocyanate, which had been dehydrated by heating for 1 hour in *vacuo* at 130° C., are converted with about
10 71.9 parts of 4,4'-diphenyl methane diisocyanate into the polyester isocyanate which is diluted with about 385 parts of dimethyl formamide to a 50% solution containing 1.41% of free isocyanate.

About 125 parts of this solution are diluted 15
with about 150 parts of dimethyl formamide and mixed with about 1.89 parts of carbodihydrazide, which is equivalent to the —NCO groups, in about 112 parts of dimethyl formamide while stirring vigorously. The substan- 20
tially 16.5% solids solution becomes more viscous (24 poises/20° C.). The solution is spun as described in Example 1. Excellent elastic filaments having the following properties are thus obtained: 25

Count: 146 den.

Tensile strength: 0.90 g./den.

Elongation: 525%

Permanent elongation: 4.8%

Modulus (100%): 0.073 g./den.

30 After boiling for about 6 hours in 5% soda solution, the filaments still have a tensile strength of 0.57 g./den with an elongation of 570% and a permanent elongation of 5%.

EXAMPLE 8

35 About 125 parts of the polyester isocyanate solution obtained as described in Example 7 are diluted with about 75 parts of dimethyl formamide and reacted with about 1.95 parts

of carbodihydrazide in about 112.5 parts of dimethyl formamide. This quantity of carbodihydrazide is 103% of the quantity calculated on —NCO content. A less viscous (40 poises/20° C.) and more concentrated (20.5%) 40
solution is obtained from which filaments having the following properties can be obtained by spinning into water at a temperature of about 90° C.:

Count: 186 den.

Tensile strength: 0.66 g./den.

45 Elongation: 500%

Permanent elongation: 5.6%

Modulus (100%): 0.072 g./den.

EXAMPLE 9

50 By reacting about 125 parts of the 50% polyester isocyanate solution of Example 7, diluted with about 75 parts of dimethyl formamide with about 1.83 parts of carbodihydrazide and 126 mg. of di-*n*-butyl amine, which

is 197% and 3% respectively of the quantity calculated on the existing —NCO groups, in about 113 parts of dimethyl formamide, the result is a solution of low viscosity (about 1 poise/20° C.) with a solid content of about 20.4%. Filaments spun from this solution as 55

described in Example 1 have a count of 184, a tensile strength of 0.60 g./den., and elongation of 550%, a permanent elongation of 3.9% and a modulus (100%) of 0.053 g./den.

EXAMPLE 10

About 300 parts of an ethylene glycol/adipic acid ester having a molecular weight of 2,000 and which had been dehydrated by heating for 1 hour *in vacuo* at about 130° C. are reacted in benzene with about 131.3 parts of 4,4'-diphenyl methane diisocyanate, the molar ratio being about 1:3.5, and subsequently diluted with about 427 parts of di-

methyl formamide into a 50% polyester isocyanate solution having an —NCO content of about 3.36%.

A solution at a temperature of about 80° C. and consisting of about 5.40 parts of carbodihydrazide in about 150 parts of dimethyl formamide is quickly stirred into about 150 parts of the first-mentioned 50% solution, diluted with about 150 parts of dimethyl formamide, a solution of low viscosity and a solid content of about 17.5% being obtained. Spinning of the filaments into hot water with a descent path of about 2 meters gives elastic filaments having the following properties:

Count: 178 den.

Tensile strength: 0.45 g./den.

Elongation: 525%

Permanent elongation: 13%

Modulus (100%): 0.094 g./den.

EXAMPLE 11

About 250 parts of a polyester of ethylene glycol and adipic acid having a molecular weight of 2,000 and dehydrated by heating for 1 hour *in vacuo* at about 130° C. and about 0.223 parts of trimethylol ethane are mixed with about 61.5 parts of a solution of 4,4'-diphenyl methane diisocyanate in about 250 ml. of benzene. The benzene is distilled off over a period of about 1 hour and then the substance is heated for about 2 hours in a boiling water bath. After stirring in about 300 parts of dimethyl formamide at about 30° C. the resulting solution has 1.38% —NCO.

About 150 parts of this solution, diluted with about 75 parts of dimethyl formamide, are transformed into a substantially 20.5% solids solution of relatively low viscosity (100 cP./20° C.) by dropwise addition of a solution at a temperature of about 60° C. and consisting of about 1.85 parts, an equivalent quantity, of carbodihydrazide in about 113 parts of dimethyl formamide. When the solution, which is formed, is spun into an aqueous precipitation bath at a temperature of about 90° C., elastic filaments having the following properties are obtained:

Count: 186 den.

Tensile strength: 0.50 g./den.

Elongation: 650%

Permanent elongation: 4%

EXAMPLE 12

About 40 parts of a polyester urethane obtained as described in Example 7 are heated with 11.67 parts of 4,4'-diphenyl - dimethylmethane diisocyanate (mol proportion 1:2.1) and 40 parts of benzene while distilling off the solvent. The mixture is heated to 96–100° C. for 2 hours. After cooling the melt 50 parts of dioxane are added. The resulting 50% solution contains 1.75% free NCO groups.

59 Parts of this 50% dioxane solution are diluted with 59 parts of dimethyl acetamide and reacted with a solution of 2.54 parts (equimolar amount) of 1,4 - butanediol - bis - hydrazine - carboxylic acid ester in 94 parts of dimethyl acetamide. The solution reaches within 2 minutes a viscosity of 22 poises/20°.

Filaments having the following properties can be obtained by spinning into water at a temperature of about 90° C.

Count: 150 den.

Tensile strength: 0.68 g./den.

Elongation: 450%

Permanent elongation: 6%

5 The 1,4 - butanediol - bis - hydrazine carb-
oxylic acid ester is prepared by slowly adding
1,4 - butanediol - bis - chlorocarbonic acid
ester to an excess of hydrazine hydrate at 0°
C. and filtering off the polymeric material.
The desired ester separates out of the filtrate
in needles m.p. 125—127° C.

EXAMPLE 13

10 500 Parts of the polyester urethane obtained
as described in Example 7 are reacted at 100°
C. for 2 hours with 146 parts of 4,4' - di-
phenyldimethylmethane diisocyanate (mol ratio
1:2.1). The product is diluted with 634 parts
15 of dimethyl formamide to a solution with
1.64% free NCO groups.

400 Parts of the polyester - isocyanate -
solution are diluted with 330 parts of dimethyl
formamide and reacted with a warm solution
20 of 6.78 parts of carbodihydrazide (equivalent

amount) in 350 parts of dimethylformamide
while stirring. The 50% solution thus obtained
is concentrated in a vacuum of 12 Torr at
70° C. to a solid content of 25%. The vis-
cosity is 175 poises/20° C.

Filaments can be obtained from the solu-
tion by spinning into hot water in accordance
to Example 1 or by spinning through a heated
tunnel. The solution is by means of a pump
spun through an 8-aperture spinneret provided
30 with holes having a diameter of 0.20 mm. into
a 4 m. tunnel heated to 175° C. Air of 180—
185° is blown into the tunnel from below. The
filament is wound at 50—150 m/minute after
talcum has been applied thereto.

If the solution is spun through a heated
tunnel at a rate of 2.4 ml/minute (a) or 4.8
ml/minute (b) and the filament wound at 150
m/minute (A) or 70 m/minute (B) filaments
40 with following properties are obtained.

	A	B
Count:	40 den.	152 den.
Tensile strength:	0.45 g/den.	0.78 g/den.
Elongation:	420%	505%
Permanent elongation:	5%	6%
Modulus 100% elongation:		0.040 g/den.

Foils which are obtained by pouring the solution onto sheets of glass and evaporating
off the solvent have the following properties:

Tensile strength: 875 kg/cm²

Elongation: 460%

Tension value at 20% elongation 11—12 kg/cm²

at 300% elongation 190 kg/cm²

Resistance to further tearing according to Graves: 50—58 kg/cm

EXAMPLE 14

45 200 Parts of the polyester urethane pre-
pared as described in Example 7 are mixed
with 33.6 parts of 1,6 - hexamethyldiisocyan-
ate (mol ratio 1:2). The mixture is heated for
3 hours to 100°. After cooling 250 parts of
50 dimethyl formamide are added. 200 Parts of
the 50% solution (NCO number 1.8) are di-
luted with 270 parts of dimethyl formamide.
14 Parts of additive (60% paste of titanium

dioxide and talcum in a ratio of 2.5:1 with
55 dimethyl formamide) are added. Then 3.85
parts of carbodihydrazide (equivalent amount)
in 200 parts of dimethyl formamide are added.
The viscosity of the 18.5% solution is in-
creased within 30 minutes to 19 poises/20°
60 C.

Filaments having the following properties
can be obtained by spinning into hot water
according to Example 1.

Count: 166 den.

Tensile strength: 0.65 g/den.

Elongation: 550%

Permanent elongation: 4%

EXAMPLE 15

100 Parts of the polyester of Example 4 are dehydrated *in vacuo* at 130° C. for 1 hour and then heated with 25 parts of 4,4'-diphenyl methane diisocyanate for 50 minutes to 110° C. 375 Parts of dimethyl formamide are added to the melt. The solution contains 0.55% free NCO.

225 Parts of the polyester isocyanate solution thus obtained are cooled to 5° C. Then a solution of 4.65 parts of 1,4 - phenylene - bis - ethyl ether carbazine acid ester in 115 parts of dimethyl formamide are added. The viscosity is increased very rapidly.

Filaments can be spun from the 21% solution having the following properties:

Count: 194 den.

Tensile strength: 0.62 g/den.

Elongation: 710%

Permanent elongation: 3.5%

Modulus (100%): 0.04 g/den.

A foil can be made by casting the solution in a layer of a thickness of 0.4 mm and evaporating the solvent. The properties are as follows:

Thickness: 0.08 mm.

Tensile strength: 550 kg/cm²

Elongation: 630%

Tension value at 20% elongation: 13.7 kg/cm²

Tension value at 300% elongation: 58.2 kg/cm²

Resistance to further tearing according to Graves: 46.0 kg/cm.

Shore hardness: 54

The 1,4 - phenylene - bis - ethyl ether carbazine acid ester is prepared by catalytic hydrogenation with Pd of 25.5 parts of dicarbobenzoxy - 1,4 - phenylene-bis-ethyl ether carbazine acid ester in 500 parts of methanol and 350 parts of dimethyl formamide. 10.6 Parts of product m.p. 176-177° C. are obtained. In the manufacture of the carbobenzoxy compound 43.5 parts of carbobenzoxy hydrazine are reacted in 130 parts of dioxane and 55 parts of pyridine at 5° C. with 42 parts of 1,4 - phenylene - bis - ethyl ether chloro carbonic acid ester in 95 parts of dioxane. The reaction mixture is acidified, the precipitate filtered off and washed free of chlorine. The crude material is recrystallised from ethanol. Melting point 157° C. The 1,4-phenylene - bis - ethyl ether chloro carbonic acid ester is obtained from 1,4 - phenylene-bis - oxethyl ether and phosgene.

EXAMPLE 16

400 Parts of the polyester of Example 4 are dehydrated *in vacuo* at 130° C. and then heated for 50 minutes to 110° C. with 71.2 parts of toluylene diisocyanate (2,4 and 2,6 isomers 65:35). 250 Parts of dry chlorobenzene are added to the melt and the solution thus obtained is diluted at 10° C. with 475 parts of dimethyl formamide. The NCO content is 1.27%.

225 Parts of the polyester isocyanate solution are cooled to 5° C. While stirring a solution of 5.95 parts of ethylene - bis - semicarbazide in 20 parts of water is added within 5 minutes. The viscosity of the solution increases rapidly.

The solution is concentrated by removing the solvent *in vacuo* to 28.7%. The viscosity is then 220 poises/20° C.

A foil can be made by casting the solution

in a layer of a thickness of 0.4 mm. and evaporating the solvent. The properties are as follows:

Thickness: 0.10 mm.

Tensile strength: 480 kg/cm²

Elongation: 660%

Tension value at 20% elongation: 23 kg/cm²

Tension value at 300% elongation: 137 kg/cm²

Resistance to further tearing according to Graves: 56 kg/cm

Shore hardness: 72

5 The ethylene - bis - semicarbazide is made as follows: 60 Parts of ethylene - bis - carbamic acid phenylester are added at 60° C. to 100 parts of hydrazine hydrate. The reaction mixture is held at 60° C. for 1 hour. After cooling the separated product is filtered off and recrystallised from water and ethanol m.p. 168° C.

15 diluted with 130 parts of dimethyl formamide. A solution of 1.06 parts of N,N¹ - piperazine dicarbonic acid dihydrazide and 4.60 parts of succinic acid dihydrazide in 20 parts of water are added at 5° C. The viscosity of the solution is increased rapidly. The solution is concentrated *in vacuo* to 35.8%, the viscosity is 180 P/20° C. 20

A foil can be made by casting the solution in a layer of thickness of 0.4 mm and evaporating the solvent. The properties are as follows: 25

EXAMPLE 17

222 Parts of the polyester isocyanate solution of Example 16 (NCO content 1.38%) are

Thickness: 0.10 mm.

Tensile strength: 185 kg/cm²

Elongation: 770%

Tension value at 20% elongation: 10.6 kg/cm²

Tension value at 300% elongation: 28.3 kg/cm²

Resistance to further tearing according to Graves: 17.3 kg/cm

30 N,N¹ - piperazine - dicarbonic acid dihydrazide is obtained by heating for 1 hour of 9718 parts of N,N¹ - piperazine - dicarbonic acid diphenyl ester in 150 parts of hydrazine hydrate and 400 parts of dimethyl formamide to 60° C. After cooling the product crystallises out, is washed with isopropanol and recrystallised from water, m.p. 213° C. 35

EXAMPLE 18

40 100 Parts of a polyacetal from 50 mol % 1,6-hexanediol, 50 mol % methylhexanediol-1,6 and formaldehyde (OH-number 164) are dehydrated *in vacuo* at 110° C. for 1 hour and then heated for 30 minutes to 100° C. with

172 parts of toluylene diisocyanate. After addition of 25 parts of 4,4¹ - diphenylmethane diisocyanate the melt is held for 30 minutes at 100° C. After dilution of the melt with 120 parts of dioxane and with 400 parts of dimethyl formamide the NCO content is 0.51%. 45

550 Parts of the polyacetal isocyanate solution are cooled to 15° C. then while stirring a solution of 3 parts of carbodihydrazide in 150 parts of dimethyl formamide (70° C.) is added. The viscosity of the solution increases strongly. The 17.2% solution thus obtained is spun to give colourless highly elastic filaments having the following properties: 55

Count: 106 den.

Tensile strength: 0.49 g/den.

Elongation: 645%

Permanent elongation: 7.6%

Modulus (300%): 0.172 g/den.

Modulus (150%): 0.098 g/den.

A foil can be made by casting the solution evaporating the solvent. The properties are as in a layer of a thickness of 0.7 mm. and follows:

5

Thickness: 0.11 mm.

Tensile strength: 390 kg/cm²

Elongation: 635%

Tension value at 20% elongation: 16.3 kg/cm²

Tension value at 300% elongation: 110.6 kg/cm²

Resistance to further tearing according to Graves: 15.6 kg/cm

Shore hardness: 52

EXAMPLE 19

10 50 Parts of a polyester acetal prepared from an adipic acid - bis - hydroxyhexylester and formaldehyde (OH-number 97) are dehydrated *in vacuo* at 110° C. for 1 hour and then heated for 30 minutes to 100° C. with 3.8 parts of toluylene diisocyanate (isomer mixture of 2.4 and 2.6 65:35). After addition of 11.05 parts of 4,4' - diphenylmethane diisocyanate 15 the melt is held for 45 minutes at 100° C. 60 Parts of absolute dioxane and then 140 parts

of dimethyl formamide are added to the melt. The NCO content of the solution is 0.48%.

20 225 Parts of the polyester acetal isocyanate solution are cooled to 15° C. While stirring a solution of 1.15 parts of carbodihydrazide in 10 parts of water and 100 parts of dimethyl formamide are added. The viscosity of the solution is increased to about 100 P/20° C. 25 The substantially 16.7% solution thus obtained was spun to give colourless highly elastic filaments having the following properties:

Count: 105 den.

Tensile strength: 0.53-g/den.

Elongation: 600%

Modulus (300%): 0.155 g/den.

Modulus (150%): 0.095 g/den.

30 A foil can be made by casting the solution orating the solvent. The properties are as in a layer of a thickness of 0.7 mm and evap- follows:

Thickness: 0.11 mm

Tensile strength: 470 kg/cm²

Elongation: 590%

Tension value at 20% elongation: 8.6 kg/cm²

Tension value at 300% elongation: 95 kg/cm²

Resistance to further tearing according to Graves: 25.6 kg/cm

Shore hardness: 55

5 It is, of course, to be understood that any of the particular reaction components such as the isocyanates, polyhydroxyl compounds or the compounds represented by the general formula set forth above and also any of the inert solvents may be substituted into the working examples for the particular compounds utilised therein and that the scope of the invention is not to be limited by these Examples.

10 WHAT WE CLAIM IS:—

15 1. A process for producing a solution suitable for the manufacture of fibres, foils and coatings, which comprises mixing a substantially linear isocyanate-modified organic compound containing terminal NCO groups (which has been prepared by reacting an excess of an organic diisocyanate with an organic compound containing active hydrogen atoms 20 which are reactive with —NCO groups and having a molecular weight of from 700 to 5,000) in an inert solvent with a dihydrazide having the general formula



25 wherein A is a CO, CS or SO₂ group; R and R¹ each represent a hydrogen atom, an alkyl radical or an aryl radical, with the proviso that at least twice in the molecule R and R¹ represent a hydrogen atom; Z is an alkylene radical, the chain of which may be interrupted by one or more hetero atoms or an arylene radical, an aralkylene radical, an NH—, NH—NH, O—Y—O or NH—Y—NH group 30 wherein Y in the last two formulae is a divalent organic radical and n is 0 or 1.

35 2. A process as claimed in claim 1, wherein the dihydrazide is employed in an amount of

from 100 mol per cent to 110 mol per cent of that required to react with the —NCO groups present.

3. A process as claimed in claim 1 or claim 2, wherein the substantially linear isocyanate-modified organic compound has been obtained by reacting an excess of an organic diisocyanate with (a) a hydroxyl polyester prepared by reacting a dihydric alcohol with a dicarboxylic acid, (b) a polyhydric polyalkylene ether, (c) a polyester amide, (d) a polyhydric polythioether, (e) a polycarbonate or (f) a polyacetal.

4. A process as claimed in any of the preceding claims, wherein the dihydrazide is carbodihydrazide.

5. A process for producing a solution suitable for the manufacture of fibres, foils and coatings, substantially as described with reference to any of the Examples.

6. A solution suitable for the manufacture of fibres, foils and coatings, when prepared by the process claimed in any of the preceding claims.

7. A process for preparing shaped articles such as fibres, foils and coatings, which comprises shaping the solution claimed in claim 6 to the desired configuration while removing the solvent therefrom.

8. A process for preparing shaped articles such as fibres, foils and coatings, substantially as described with reference to any of the Examples.

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